Novel Methods of Synthesis of Dibenzo[3n]crown-n and Their Cation Binding Studied by Fluorescence Spectroscopy. Part V *

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Abstract

The dibenzo[3n]crown-n were synthesised starting from bis[2-(*o*-hydroxyphenoxy)ethyl]ether obtained from bis[2-(*o*-formylphenoxy)ethyl]ether via Baeyer-Villiger oxidation in H_2O_2/CH_3COOH in a good yield. The cyclic condensation of bis[2-(*o*-hydroxyphenoxy)ethyl]ether with tri- and tetraethylene glycol bisdichlorides and the bisditosylate of pentaethylene glycol in DMF/Me_2CO_3 afforded the large cyclic ethers of dibenzo[21]crown-7, dibenzo[24]crown-8 and dibenzo[27]crown-9. The structures were analysed with IR, ^1H NMR, ^{13}C NMR and low-resolution mass spectroscopy methods. The Na^+, K^+, Rb^+ and Cs^+ cations' recognition of the molecules were conducted with steady-state fluorescence spectroscopy. The 1:1 association constants, K_a, in acetonitrile were estimated. Dibenzo[21]crown-7 was the best both for K^+ and Rb^+ binding but showed too small an effect on Cs^+. Dibenzo[24]crown-8 exhibited the binding power in the order of $Rb^+ > K^+ > Na^+ > Cs^+$. However, dibenzo[27]crown-9 displayed marked binding with only K^+ but not with Rb^+ or with Cs^+ cations probably due to the heavy atom effect of fluorescence quenching.

Introduction

Dibenzo macrocyclic ethers with different length of oxyethylene bridges between the *o, o'*-dioxydibenzo groups are less known due to limited preparation methods [1–8]. Primarily, Pedersen developed the preparation method of the polyglycols with bis-*o*-hydroxyphenoxy terminals by protecting one of the phenolic dihydroxyl group with the 2,3-dihydropyrano group, condensing with the dihalide of polyglycols which was then hydrolysed in acid for hydroxyl liberation [1]. Another method of preparation of the mono benzyl derivative of the catechol followed by the polyethylene glycol condensation and catalytic hydrogenolysis of the benzyl groups that afforded the (*o, o'*-dihydroxy)diphenoxy terminals has been reported [5–8]. We have, however, recently developed a high yield synthesis method of 1,2-bis(*o*-hydroxyphenoxy)ethane and similar podands starting from *o*-hydroxy benzaldehyde. The large dibenzo[3n]crown-n, (n = 5–7), macrocycles were, therefore synthesised by cyclic condensation of such podands as reported [9].

In the present work we prepared the dibenzo[3n]crown-n, (n = 7–9) starting from salicylaldehyde, which was condensed with bis(2-chlorodiethyl)ether to form the bis[2-(*o*-formylphenoxy)]ethyl ether, [10]. Baeyer-Villiger oxidation [11] of this product with H_2O_2 in CH_3COOH gave a good yield of bis[2-(*o*-hydroxyphenoxy) ethyl] ether, [4, 5] which led us to prepare the large dibenzo[3n]crown-n, [3, 5–7] in satisfactory yields, Scheme 1.

The macrocycles with different oxyethylene bridges between the bis(*o, o'*-dioxybenzo) groups of 7–9 oxygens, **4a–4c**, displayed interesting cation binding behaviours. They have been already reported to form crystalline complexes with cations [3, 5–7] as [18]crown-6 does with K^+ and Rb^+ [12, 13].

Thus, we studied the cationic recognition of such crown ethers with fluorescence spectroscopy [14], although cationic recognition of macrocyclic ethers has been investigated by several analytical methods [15]. Fluorescence spectroscopy is quite practical since the fluorescence and phosphorescence life times of the $\pi \rightarrow \pi^*$ responsive transitions are induced by the cations [16].

Our interest in macrocyclic fluorophores with aromatic benzo- and naphtho-groups of moderate fluorescence quantum yields as well as coumarin and anthraquinone groups of strong chromo- and fluorophore moieties have been reported [9, 14].

Experimental

Salicylaldehyde, bis(2-chloroethyl)ether, pentaethylene glycol ditosylate and CH_3CN were from Fluka or Merck unless otherwise cited. $RbClO_4$ and CsOH used to form $CsClO_4$ were from Acros. The polyglycol dichlorides were available to us from our earlier work [14]. EI mass spectra were recorded on a Fisons VG-Zabspec instrument using the direct inlet. IR spectra were recorded as KBr pellets on a Jasco FTIR spectrometer, model 5300. 400 MHz ^1H NMR and 100 MHz ^{13}C NMR spectra were obtained on a Bruker

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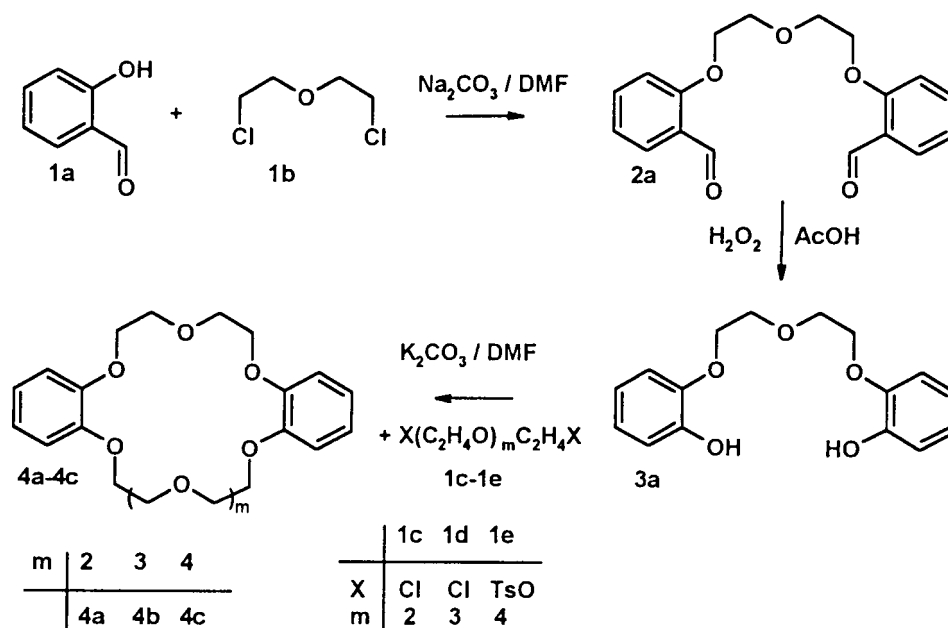
Scheme 1.

Table 1. Complexing fluorescence data of **4a**/KClO$_4$ in CH$_3$CN using Equation (3), where log K$_a$ = 4.455, correl. coef. = 0.9988, y-int. = −0.0287

Ion conc. (10^5 mol/L)	Intensity I$_x$	(I$_{max}$−I$_x$)	(I$_x$−I$_o$)	(I$_{max}$−I$_x$)/ (I$_x$−I$_o$)
4.95	360.0	50.0	79.0	1.58
7.39	370.5	39.5	89.5	2.67
1.22	383.0	27.0	102.0	3.78
1.69	389.0	21.0	108.0	5.14
1.92	390.0	19.6	109.4	5.58
2.15	392.5	17.5	111.5	6.37
2.38	394.5	15.5	113.5	7.32
2.83	396.4	13.6	115.0	8.49
3.05	397.7	12.3	116.0	9.49
3.49	399.0	11.0	118.0	11.73

Table 2. Cation association constants, log K$_a$, of dibenzo[3n]crown-n, in acetonitrile obtained from fluorescence data, ($\lambda_{excitationmax}$ = 278–280 nm, $\lambda_{emissionmax}$ = 308–310 nm)

Macrocycle*	Cation	log K$_a$	−ΔG (kJ/M)	I$_o$/I$_{max}$
dbz21c7, 4a	Na$^+$	2.56	13.38	348/080
dbz21c7, 4a	K$^+$	4.46	23.18	281/410
dbz21c7, 4a	Rb$^+$	4.38	22.80	240/410
dbz21c7, 4a	Cs$^+$	2<	–	–
dbz24c8, 4b	Na$^+$	3.37	17.51	255/170
dbz24c8, 4b	K$^+$	2.62	13.64	225/170
dbz24c8, 4b	Rb$^+$	3.87	20.11	240/265
dbz24c8, 4b	Cs$^+$	3.10	16.14	240/290
dbz27c9, 4c	Na$^+$	2<	–	–
dbz27c9, 4c	K$^+$	2.43	12.63	195/273
dbz27c9, 4c	Rb$^+$	2.81	14.60	289/400
dbz27c9, 4c	Cs$^+$	3.07	16.00	267/220
Benzoquinone*	–	–		I$_o$ = 640**

* Conc. 5.0 × 10^{-3} mol/L.
** Conc 2.0 × 10^{-3} mol/L.

CPX-400 NMR spectrometer using TMS as an internal reference. The steady state fluorescence measurements were carried out with a JASCO FP-750 spectrofluorometer using the standard software. The measuring unit is equipped with a thermostated fluorescence cell compartment and a magnetic stirrer to study at 25.0 ± 0.1 °C. The salt solutions in dry CH$_3$CN (5.0 × 10^{-3} mol/L) were added stepwise to the stirred macrocyclic ether in dry CH$_3$CN, (2.00 mL), in a 10-mm quartz cell and the emission intensities were measured. Association constants, K$_a$ were calculated with Excel, (MS Office), using least-squares data according to Equation (3). I$_{max}$ and I$_o$ values were simulated to approach the highest correlation coefficient and the minimum y-intercept of a line of Equation (3), (see Table 1). Resulting log K$_a$, (±0.1), Gibbs enthalpies, ΔG (±0.1), emission intensities of complexes and benzoquinone, (2 × 10^{-3} mol/L) as a reference are displayed in Table 2, (see Figures 1 and 2).
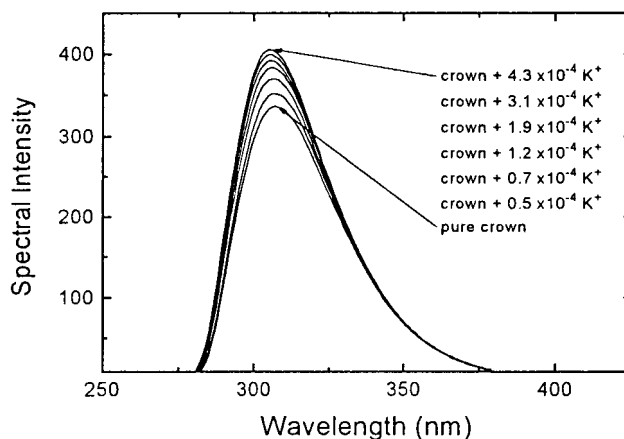

Figure 1. Emission fluorescence spectra of dibenzo[21]crown-7/**4a**, in the presence of various KClO$_4$ concentrations, (ML^{-1}) in CH$_3$CN at 25 °C, ($\lambda_{excitationmax}$ = 278 nm).
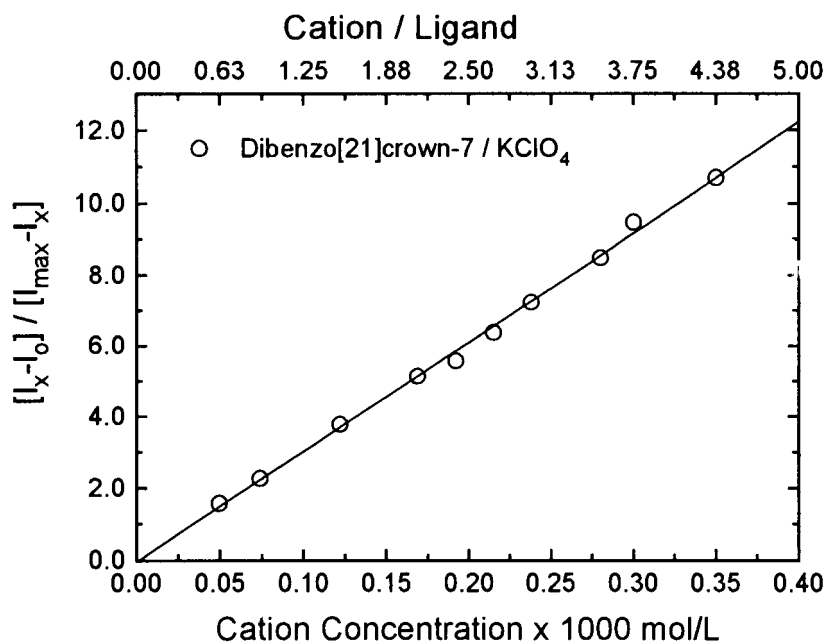
Cation / Ligand

Figure 2. Plot of the 1/1 complex of dibenzo[21]crown-7/**4a** according to Equation (3) (see Table 1).

Organic synthesis

Bis[2-(o-formylphenoxy)ethyl]ether (2a); In a three necked flask (500 mL) Na$_2$CO$_3$ (36.4 g, 340 mmol), water (35 mL), DMF (100 mL) and salicylaldehyde, (**1a**) (41.5 g, 340.0 mmol) were mixed and heated while stirring. Bis(2-chloroethyl)ether, (**1b**) (25.2 g, 170.0 mmol) in DMF (20 mL) was added to the flask in 3 h. The mixture was heated at 90–95 °C for 48–54 h, cooled then acidified with HCl (80 mL, 37%) and water (200 mL). The filtered residue was dissolved in CHCl$_3$ (200 mL) boiled with charcoal (2 g) and dried on Al$_2$O$_3$ (basic, 7.5 g). The evaporated solution was eluted from Al$_2$O$_3$ (basic, 110 g) with CHCl$_3$ (3x50 ml). (**2a**) 18.8 g, 35% yield, M.p. 73 °C. IR: ν = 3075 (Ar-H), 2945 (C-H), 2766 (CHO), 1681 (C=O), 1592, 1482 (C=C), 1234 (Ar-O-C), 1042 (C-O-C), 836 (C-C), 760 (C-H) cm^{-1}; ^{1}H NMR 400 MHz (CDCl$_3$/TMS): δ = 3.98(4H, t, 2CH$_2$O), 4.26(4H, t, 2CH$_2$O), 6.99(4H, t, Ar), 7.51(2H, t, Ar), 7.81(2H, t, Ar), 10.44(2H, s, CHO) ppm; ^{13}C NMR 100 MHz (CHCl$_3$/TMS) δ = 69.2, 70.7, 114.0, 122.2, 126.3, 129.6, 137.1, 162.5, 191.1 ppm; Mass (m/z): 314(M$^+$), 197, 121.

Bis[2-(o-hydroxyphenoxy)ethyl]ether (3a); In a flask (500 mL) bis[2-(o-formylphenoxy)ethyl]ether, (**2a**) (1.46 g, 4.6 mmol), and acetic acid (15 mL, 250 mmol) were warmed at 40 °C on a water bath while stirring. To this mixture, H$_2$O$_2$, (30%, 5 mL) was added cautiously in 1/2 h, (CAUTION, fume cupboard). The reaction mixture was stirred at 40 °C for 24 h and allowed to cool to –10 °C for 24–48 h which formed colourless large cubic crystals. (**3a**) 0.33 g, 24.5% yield. M.p. 95–100 °C. IR: ν = 3335 (OH), 3068 (Ar-H), 2947 (C-H), 1613, 1516 (C=C), 1272, 1224 (Ar-O-C), 1127 (C-O-C), 958 (C-C), 763 (Ar-H) cm^{-1}; ^{1}H NMR 400 MHz (CDCl$_3$/TMS): δ = 3.84(4H, t, 2CH$_2$O), 4.12(4H, t, 2CH$_2$O), 6.93(8H, m, Ar), 8.90(2H, s, OH) ppm; ^{13}C NMR

100 MHz (DMSO-d$_6$/TMS): δ = 70.0, 70.5, 116.1, 117.1, 120.8, 123.4, 147.7, 148.7 ppm; Mass (m/z): 290(M$^+$), 181, 137, 109.

Dibenzo[b,k]6,7,9,10,12,13,20,21,23,24-decahydro-1,4,7, 10,13,16,19-heptaoxacycloheneicosin. (Dibenzo[21]-crown-7) (4a); In a flask (100 mL), bis[2-(o-hydroxyphenoxy)ethyl] ether, (**3a**) (1.43 g, 4.93 mmol), DMSO (10 mL) and K$_2$CO$_3$ (1.40 g, 10.0 mmol) were heated while stirring at 70–80 °C. To this mixture 1,8-dichloro-3,6-dioxaoctane (**1c**) (0.95 g, 5.08 mmol) in DMF (5 mL) were added in 2 h and the mixture was heated at 90–100 °C for 90–100 h. The solution was acidified with HCl (25 mL, 0.2 N) and water (200 mL) was extracted with CH$_2$Cl$_2$ (4 × 30 mL) and the organic layer was dried with Al$_2$O$_3$ (basic, 3 g). The raw product was chromatographed on Al$_2$O$_3$ (50 g, basic) with CH$_2$Cl$_2$ (4 × 40 mL) (**4a**), 0.84 g, 42% yield, M.p. 114–116 °C. IR: ν = 3050 (Ar-H), 2950 (C-H), 1613, 1516, 1467 (C=C), 1273 (Ar-O-C), 1127 (C-O-C), 958 (C-C), 763 (Ar-H) cm^{-1}; ^{1}H NMR 400 MHz (CDCl$_3$/TMS): δ = 3.86(4H, s, 2CH$_2$O), 3.89(4H, t, 2CH$_2$O), 4.02 (4H, m, 2CH$_2$O), 4.14(4H, t, 2CH$_2$O), 4.19(4H, t, 4CH$_2$O), 6.95(8H, m, ArH) ppm; ^{13}C NMR 100 MHz (CDCl$_3$/TMS): δ = 70.4, 70.5, 70.6, 70.9, 71.2, 72.2, 115.3, 116.5, 122.6, 123.0 ppm; Mass (m/z): 404(M$^+$), 279, 167, 136, 121.

Dibenzo[b,k]6,7,9,10,12,13,15,16,23,24,26,27-dodecahy-dro-1,4,7,10,13,16,19,22-octaoxacylotetracosin (Dibenzo [24]crown-8) (4b), bis[2-(o-hydroxyphenoxy)ethyl] ether, (**3a**) (1.06 g, 3.65 mmol), K$_2$CO$_3$ (1.19 g, 8.52 mmol) and DMSO (10 mL) were mixed in a flask (50 mL) and stirred while heated at 90–95 °C. To the mixture 1,11-dichloro-3,6,9-trioxaundecane (**1d**) (1.0 g, 4.32 mmol) in DMF (10 mL) was added in 3 h and heated for 90–100 h. The mixture was cooled and diluted with water (200 mL) and HCl (10

mL, 0.2 N). The product was separated with CH_2Cl_2 (4 × 30 mL) extraction and the organic layer was dried on Al_2O_3 (basic, 4.0 g) then chromatographed on Al_2O_3 (neutral, 15 g) with $CHCl_3$ (3 × 30 mL). (4b), 0.15 g 18% yield, colourless leafs. M.p. 60–61 °C. IR: ν = 3055 (Ar-H), 2935 (C-H), 1596, 1516 (C=C), 1253 (Ar-O-C), 1152 (C-O-C), 947 (C-C), 744 (Ar-H) cm^{-1}; ^1H NMR 400 MHz (CDCl$_3$/TMS): δ = 3.70(4H, t, 2CH$_2$O), 3.75(4H, t, 2CH$_2$O), 3.86(4H, t, 2CH$_2$O), 3.98(4H, t, 2CH$_2$O), 4.13(4H, t, 2CH$_2$O), 4.19(4H, t, 2CH$_2$O), 6 .90(8H, m, Ar) ppm; ^{13}C NMR 100 MHz (CDCl$_3$ /TMS): δ = 70.1, 70.6, 70.7, 71.2, 71.6, 72.0, 115.5, 116.9, 122.6, 123.0, 150.4, 150.8 ppm; Mass (m/z): 448 (M$^+$), 279, 167, 149, 136.

Dibenzo[b,k]6,7,9,10,12,13,15,16,18,19,26,27,29,30-tetradecahydro-1,4,7,10,13,16,19,22,25-nonaoxacycloheptacosin (Dibenzo[27]crown-9) (4c); In a flask (100 mL), bis[2-(o-hydroxyphenoxy)ethyl] ether, (3a) (0.58 g, 2 mmol), DMF (15 mL) and K_2CO_3 (0.55 g, 4 mmol), pentaethylene glycol ditosylate (1e) (1.10 g, 2.01 mmol) were heated while stirring for 95–100 h at 90 °C. The mixture was then cooled, diluted with water (200 mL) and HCl (10 mL, 0.2 N). The raw product was separated with $CHCl_3$ (3 × 40 mL) extraction. The organic layer was dried with Al_2O_3, (basic, 3.0 g). The raw product was chromatographed on Al_2O_3 (basic, 10.0 g) with CH_2Cl_2 (4 × 45 mL). (4c), 0.15 g. 15% yield, white cubic crystals, M.p. 84–87 °C. IR: ν = 3057 (Ar-H), 2926 (C-H), 1595(C=C), 1250(Ar-O-C), 1121(C-O-C), 932(C-C), 743(Ar-H) cm^{-1}; ^1H NMR 400 MHz (CDCl$_3$/TMS): δ = 3.87(4H, s, 2CH$_2$O), 3.66(4H, t, 2CH$_2$O), 3.75(4H, t, 2CH$_2$O), 3.86(4H, t, 2CH$_2$O), 3.98(4H, t, 2CH$_2$O), 4.14(4H, t, 2CH$_2$O), 4.19(4H, t, 2CH$_2$O), 6.94(8H, m, Ar) ppm; ^{13}C NMR 100 MHz (CDCl$_3$ /TMS): δ = 69.8, 70.3, 70.5, 70.7, 70.9, 71.2, 72.2, 115.5, 116.6, 122.7, 122.9, 150.4, 150.7 ppm; Mass (m/z): 492 (M$^+$), 448, 404, 360, 136.

Cationic recognition using fluorescence spectroscopy

The macrocyclic-metal association in CH_3CN was estimated by measuring the steady-state fluorescence emission intensities of the fluorophore macrocycles in the presence of various initial cation concentrations, [M$_o$]. The 1:1 association constants, K$_a$, of the complex, [M$^+$L] in the mole balance of cation concentration, [M$^+$], and crown ether, [L] were determined, Equations (1)–(3). The 1:1 association constants, K$_a$, were estimated according to Equation (3) due to the observed complexation altered fluorescence data [9, 14].

$$L + M^+ \rightleftharpoons M^+L \qquad (1)$$

$$K_a = [M^+L]/[L][M^+] \qquad (2)$$

$$(I_x - I_o)/(I_{max} - I_x) = K_a [M_o]. \qquad (3)$$

The observed intensity of steady-state fluorescence of complex mixtures involves the free, I$_o$ and the 1:1 complex,

I_{max} intensities [16]. The emission intensities of the free and cation complexed fluorophore, I$_o$ and I$_x$ (10^{-4} mol/L) were measured at λ = 308–310 nm using the fluorescence excitation maximum at λ = 278 nm upon the addition of the appropriate amount of the cation solution (Figure 1).

Results and discussion

The product 2a obtained from 1a and 1b in 35–37% yields was converted to 3a in 24–25% yields in the presence of H_2O_2/CH_3COOH. 3a reacted with 1c–1e to yield 4a, 4b and 4c respectively with yields of 15–42% (see Scheme 1). However, the reported method was not very successful for the hydroxylation of bis[2-(1-formylnaphthoxy)-ethyl] ether in H_2O_2/CH_3COOH due to the poor solubility of such naphthalene derivatives [9].

However, 2a has been prepared before in DMSO [10]. 3a has been prepared from catechol and 1b [4]. 4a and 4b have been primarily synthesised in ethanol as reported in the literature [3].

The recognition of Na$^+$, K$^+$, Rb$^+$ and Cs$^+$ perchlorates by 4a–4c were studied with steady-state fluorescence spectroscopy and we report the 1:1 association constants of the macrocycle-cation complexes in CH_3CN at 25 °C.

The role of the two electron withdrawing aromatic moieties in reducing the electron donation of the aromatic terminal oxygens as well as reducing macrocycle flexibility is indicated in the present work. However, macrocyclic backbone conformations of large oxygen numbers could be oriented according to the metal coordination ability, although the small groups are rather rigid [2, 3, 17]. Cations encapsulated by the seven to nine oxygen atoms seem to be achieved to maximum complex stability just by K$^+$ for dibenzo[21]crown-7, 4a, Figure 2, and by Rb$^+$ as well, but not by Cs$^+$ with dibenzo[24]crown-8, 4b, and dibenzo[27]crown-9, 4c [3, 9, 18–20]. This is due to the fact that the stability of the metal coordination decreases while the cation diameters are increased which may become less significant [2, 3]. However, note that K$^+$ has been shown to give the strongest complex with nonactin, a very large naturally occurring tetralactone macrocycle [21]. This is probably due to the fact that K$^+$ could be well located in an adequately folded crown but Cs$^+$ is still large to be centrally located even in the largest macrocyclic pseudo cavity [22].

The interaction of the oxygen dipoles of dibenzo macrocycles with Cs$^+$ are not sufficient to bind the large cations and, therefore, small macrocycles of C$_2$ symmetry are more capable to form 2/1 ligand/cation complexes. In fact, the results showed that potassium is the best to bind macrocycles, 4a–4c, due to its well known coordination ability [2, 19]. The C$_4$ symmetry of the dibenzo macrocycles is more strained than the C$_2$ symmetry of crowns to adapt their conformation for ion binding. The results in acetonitrile, were mostly in agreement with the earlier reports obtained with calorimetry and ion selective electrodes (ISE) studied in methanol which are represented in Table 3 [3, 8, 17].

On the other hand, photophysical interactions are more complicated than those of the chemical interactions between

Table 3. The reported 1:1 association constants of dibenzo[3n]crown-n complexes [3, 8, 17]

Compound	log K^a (K^+)	log K^a (Rb^+)	log K^a (Cs^+)	Solvent	Method	Ref.
Benzo[18]crown-6 (2,2)*	5.10	4.36	3.55	CH_3OH	Calorimetry	(8)
Dibenzo[21]crown-7 (2,3)	4.19	4.25	–	CH_3OH	Calorimetry	(8)
Dibenzo[21]crown-7 (2,3)	–	4.40	4.20	CH_3OH	ISE	(3a)
Dibenzo[24]crown-8 (2,4)	3.45	3.80	–	CH_3OH	ISE	(3b)
Dibenzo[24]crown-8 (3,3)	2.42	2.55	2.48	CH_3OH/H_2O**	Calorimetry	(17)
Dibenzo[27]crown-9 (3,4)	2.86	–	1.42	CH_3OH/H_2O**	Calorimetry	(17)

* Number of oxyethylenes in the aliphatic bridges.
**Methanol/water (70/30).

the fluoroionophores and the cations. The intersystem cross-ing, $T_1 \rightarrow S_0$, decay rate is, in particular, induced by bound cations depending on the charge density of unpaired oxygen electrons which are delocalised on polar cations upon complex formation [14, 16, 18]. However, conformational restrictions as discussed above reduce the fluorescence yields of nonradiative decay, the $S_1 \rightarrow S_0$ rate was reported from the life time measurements of [24]crown-8/alkali complexes, [21] where the $T_1 \rightarrow S_0$ rates of Cs^+ and Rb^+ complexes are high for six oxygen macrocycles due to the contribution of the heavy cation effect. On the other hand, a $Cs^+ - \pi$ interaction is often observed to produce an internal quenching which may diminish the over all intensity of the $\pi \rightarrow \pi^*$ transitions even though complexes are stable enough.

Acknowledgement

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